

The Crystal Structure of *Trans* Potassium Dioxalatodiaquo-Chromiate

$K[Cr(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$

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The method of double Fourier series has been applied to determine the crystal structure of *trans*-potassium dioxalatodiaquo-chromiate, $K[Cr(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$. Projections of the electron density on two axial planes have been made, and the parameters of the structure have been measured.

The crystal is monoclinic, space group $P2/c$. The unit cell, of dimensions

$$a = 7.85, \quad b = 5.72, \quad c = 13.88 \text{ \AA.}, \quad \beta = 109^\circ 30',$$

contains only two formula units.

The two oxalato groups of the complex ion $[Cr(C_2O_4)_2(H_2O)_2]$ lie in a single plane. The two water molecules of the complex ion are perpendicular to this plane. The dimensions of the complex ion are given.

A discussion of the packing of the formula units is given. The main forces holding the structure together are due to both ionic and hydrogen bonding, and these bonds are discussed.

Morphology and optical properties

The material used in this investigation was prepared by Dr S. Shuttleworth of the Leather Industries Research Institute, Grahamstown, following the method described by Werner (1914). The crystals are dark red in colour with brilliantly reflecting faces, but they show a very pronounced tendency to intergrow so that it is difficult to isolate good, clear, single crystals for X-ray and optical examination. The crystals are monoclinic and very hard, making it difficult to cut or cleave them.

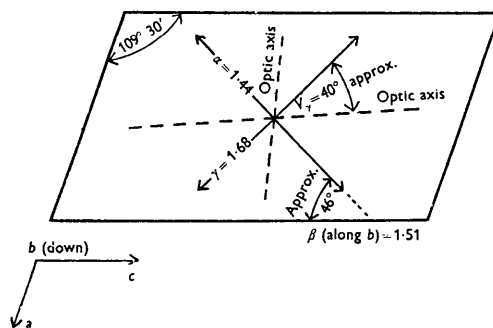


Fig. 1. Directions of refractive indices and optic axes in the unit cell.

Good goniometer measurements were obtained from some of the smaller specimens, as the faces (001) and $(00\bar{1})$ and the prism faces $\{011\}$ round the zone $[100]$, as well as the (010) , $(0\bar{1}0)$, (100) and $(\bar{1}00)$ faces, occasionally develop in the same specimen. Such measurements lead to $\beta = 109^\circ 30'$.

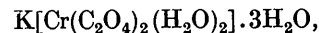
As an aid in guessing a provisional structure, refractive indices were determined by the immersion method. The optical data are summarized in Fig. 1.

The unit cell and space group

Oscillation photographs were taken using filtered Cu $K\alpha$ radiation, and from these the axial lengths were determined. The dimensions of the unit cell are

$$a = 7.85, \quad b = 5.72, \quad c = 13.88 \text{ \AA.}, \quad \beta = 109^\circ 30'.$$

The density of the crystal, determined by the method of flotation, is 1.98 g.cm.^{-3} . The unit cell, therefore, contains two of the formula units



corresponding to a true density of 2.02 g.cm.^{-3} .

General reflexions hkl occur in all orders, so that the unit cell having the above dimensions is primitive. Reflexions $h0l$ and $00l$ are present only with l even. There are no other restrictions. Oscillation photographs taken about the a axis, with the b axis at the centre of oscillation, indicated the presence of a twofold rotation axis parallel to b . The space group is therefore uniquely fixed as $P2/c-C_{2h}^4$.

Preliminary estimate of the structure

In the space group $P2/c$ the general position is fourfold, and, since there are only two of the formula units $K[Cr(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$ in the unit cell, it follows that the potassium and chromium atoms, as well as one of the three molecules of water of crystallization, must lie in special positions. These special positions are the symmetry centres and twofold axes of the space group $P2/c$. It is, however, not possible at this stage to say with certainty which of these special positions are occupied by the chromium atoms and which by potassium ions and water molecules, as various possibilities exist.

Assuming a planar symmetrical configuration for the $\text{Cr}(\text{C}_2\text{O}_4)_2$ groups, and distances between carbon and oxygen atoms found by Zachariassen (1934) and by Robertson & Woodward (1936) for oxalic acid dihydrate, solid three-dimensional models were made and were packed into the unit cell with due regard to the symmetry. If one assumes that the chromium atoms in the $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ complex ions lie on the twofold axes of the space group, then this would imply that these complex ions themselves must have a twofold axis. The axial length of the unit cell along the b direction is only 5.72 Å., whereas the dimension of a complex ion perpendicular to the plane of the $(\text{C}_2\text{O}_4)_2$ groups was calculated to be about 6.7 Å., so there seems to be not enough space in the unit cell to pack a complex ion $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ with its possible twofold axis, perpendicular to the $(\text{C}_2\text{O}_4)_2$ planes, in coincidence with that of the space group. This argument is confirmed by refractive index considerations, for such an arrangement would lead one to expect that the smallest index (α) would be along the b direction, as the light will then be vibrating perpendicular to the oxalato planes, whereas it is found that β is along the b axis.

A second possibility is to have the shorter symmetry axis, which lies in the planes of the oxalato groups, in coincidence with a twofold axis of the space group. In this case there is room to pack the complex ions into the available space. Such an arrangement would entail a large refractive index along b , as the light would then be vibrating in the oxalato planes. It is found, however, that the index along b is the medium one, so that refractive index considerations again seem to negative this arrangement. Furthermore, still assuming a planar symmetrical configuration for the $\text{Cr}(\text{C}_2\text{O}_4)_2$ groups, the fact that the chromium atoms must lie on the twofold axes of the space group places the stringent condition on such groups that no tilts are possible. This is a condition which is very rarely encountered in such complex crystals.

A better alternative seems to be for the chromium atoms in the complex ions to occupy the symmetry centres of the space group. The potassium ions will then probably lie on the twofold axes. In this case the oxalato groups need not be planar or symmetrical and any degree of tilt is possible, so that the entire arrangement in the unit cell becomes much more flexible. With this arrangement it was possible to pack our solid models into the space available in such a way as to conform to symmetry conditions and to refractive index considerations. It was, therefore, decided to adopt this latter alternative in the preliminary trials for a structural solution.

For further confirmation of the positions occupied in the unit cell by the potassium and chromium atoms, it was considered necessary to make a Patterson-Harker section (Harker, 1936). For this purpose equi-inclination Weissenberg photographs were taken for a small crystal rotating about its b axis, using Mo $K\alpha$ radiation.

The values of $|F(hkl)|^2$ for all spectra on these films were calculated, and with these terms as coefficients, the special series $P(u, 0, w)$ was evaluated. This special case of the Patterson-Harker series gave the distances and directions of the heavy atoms from a twofold axis. The section finally obtained indicated a strong peak at the origin as well as a second strong peak and also a number of weaker peaks, so that it was possible to fix the distance between the potassium and chromium atoms, as well as the direction between them, which was found to be parallel to the direction of the (102) planes in the crystal.

Combining the results obtained from refractive index measurements, packing considerations and the Patterson-Harker section, a preliminary structure as outlined below was assumed. Taking the origin of co-ordinates as given in *Internationale Tabellen* for the space group $P2/c$, the chromium atom lies at a symmetry centre $(\frac{1}{2}, \frac{1}{2}, 0)$ and the potassium ion lies on a twofold axis at $(0, y, \frac{1}{4})$, with the oxalato-groups directed from the chromium towards the potassium ions (Fig. 3).

Relative intensity measurements

In order to make a two-dimensional Fourier analysis of the structure, it was necessary to determine the structure factors $|F(h0l)|$ and $|F(0kl)|$ for all spectra of appreciable strength. For this purpose a crystal specimen of approximately cubic dimensions with a side of <0.2 mm. was used. It was alternately mounted for rotation about the a and b axes, and in these positions zero-layer Weissenberg photographs were taken using filtered Mo $K\alpha$ radiation. For such small crystals it was assumed that corrections for absorption would not be appreciable. Such corrections were neglected during this work, as the intensities of the various reflexions could not be measured with any great accuracy.

As no ionization spectrometer or integrating photometer was available, the intensities of the relevant spectra were estimated visually by comparing them with a set of previously calibrated intensity spots of approximately the same dimensions. The intensities were also measured on a densichron modified for this purpose, and the results obtained by these two methods were found to be reasonably consistent. The intensities thus measured were assumed to be proportional to the integrated intensities of the corresponding spectra, and the way in which it proved to be possible to relate observed and calculated intensities when once the nature of the structure was known showed that no great errors had been introduced by making this assumption.

The Fourier synthesis of the structure

For an accurate determination of the structure the method of double Fourier series was used (Bragg, 1929). The preliminary structure promised best resolution of the atoms when projected on the ac plane in a direction parallel to b , whilst a projection on the bc plane parallel to a promised sufficient information to fix most of the

y co-ordinates. The structure factors were calculated using the standard expressions for the space group $P2_1/c$.

A rough temperature correction for the various atomic scattering factors was made, and used in all subsequent structure-factor calculations. For carbon the values obtained by Robertson (1935) for anthracene were used. For oxygen the values of James & Brindley (1931) were reduced in the same ratio as that by which Robertson's values for carbon differed from those of James & Brindley. For K^+ the f values given by James & Brindley (1931) and for Cr the f values given by Thomas-Fermi were multiplied by the Debye-Waller temperature factor $\exp[-B(\sin\theta/\lambda)^2]$, where it was estimated that for Cr and K^+ the values of B in the factor given above were 0.4 and 0.3 respectively.

Evaluation of the Fourier series for the projection on the ac plane

Since the Patterson section fixed with certainty only the positions of the potassium and the chromium atoms in the ac projection, it was decided as a first approximation to calculate the signs of $F(h0l)$ and $F(\bar{h}0l)$ for the stronger half of the observed spectra only, and in making these calculations to use only the co-ordinates of the potassium and chromium atoms. It seemed reasonable to expect that the signs of the structure factors for a complete unit would be determined mainly by these two heavy atoms, particularly in those cases where they happen to scatter in phase. Using the calculated signs and the observed values for $F(h0l)$ and $F(\bar{h}0l)$, the double series $\sigma(x, z)$ was evaluated, the method used being substantially that described by Lipson & Beevers (1936). The projection so obtained showed the heavy chromium and potassium peaks quite clearly resolved, together with the faint outlines of other atoms in the unit. Using this projection, together with our solid models for the $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ complex, it was possible to assign approximate co-ordinates to the rest of the atoms in the complex ion. Furthermore, peaks due to the three molecules of water of crystallization were also beginning to show up in this projection, with one water molecule in a general position and the other on a twofold axis, thus accounting for the six molecules of water of crystallization in the unit cell, and confirming our preliminary ideas.

The structure factors were recalculated using these estimated co-ordinates for all the atoms, and this time all the observed spectra were included. The series was evaluated for a second time and the projection was now much clearer. In this way by successive approximations a projection was finally obtained where none of the structure factors changed sign. The contour diagram drawn from the final values of $\sigma(x, z)$ is shown in Fig. 2, which may be interpreted with the aid of Fig. 3.

The observed and calculated structure factors are shown in Table 1. (Structure factors not included in this table have zero observed values, and their correspond-

ing calculated values were small.) The agreement on the whole is quite good, and generally it is only for the high-order spectra with $\sin\theta$ greater than 0.5 that any serious discrepancies are found; in such cases the observed values are nearly always too small. Since no differential corrections for temperature motion for the different spectra were made, one would expect the

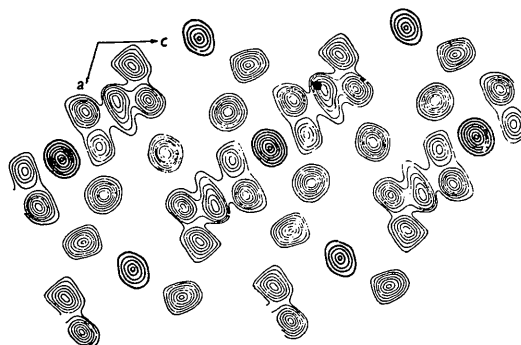


Fig. 2. Fourier projection of the structure in the direction of the b axis on to the ac plane. Contours at arbitrary intervals. The heavy contour lines, drawn at higher intervals, indicate the positions of the potassium and the chromium atoms.

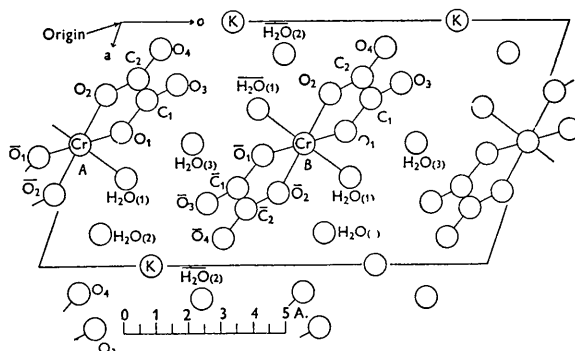


Fig. 3. Projection of the structure in the direction of the b axis on to the ac plane. Units marked B are derived from those marked A by the operation of a glide plane parallel to (010) .

observed values for those spectra, particularly the higher orders, which are most affected by thermal vibration, to be somewhat lower than the calculated values. Finally, it may be pointed out that, with few exceptions, the final signs calculated for $F(h0l)$ and $F(\bar{h}0l)$ were the same as those calculated using only the chromium and potassium co-ordinates.

Evaluation of the Fourier series for the projection on the bc plane

From the final ac projection it was possible to fix the x and z co-ordinates of all the atoms in a formula unit with a fair degree of accuracy, except perhaps in the case of the carbon atoms in the oxalato groups, as such atoms were not quite resolved. Still assuming a planar configuration for the oxalato groups, the ac projection indicated that the oxalato planes were inclined at approximately 60° to the ac plane. It was also evident from the ac projection that there was a small tilt on

the $[Cr(C_2O_4)_2(H_2O)_2]$ ions such that the long axis of such an ion made an angle of approximately 10° with the ac plane. It was possible from the ac projection to determine the directions of inclination and tilt of the complex ions, and hence when using this projection in conjunction with our models, approximate y coordinates could be assigned to all the atoms in the above groups.

The potassium ion, although forced to lie on the twofold axis, could have any y co-ordinate along this axis. Furthermore, it was found that the chromium atoms made no contribution to $F(0kl)$ when l was odd, and that these structure factors were almost entirely responsible for determining the positions of the potassium ions in the bc projection. Before attempting to evaluate the series it was therefore necessary to know

Table 1. *Calculated and observed structure factors*

hkl	$F_{calc.}$	$F_{obs.}$	hkl	$F_{calc.}$	$F_{obs.}$	hkl	$F_{calc.}$	$F_{obs.}$
100	- 41	40	$\bar{5}04$	+ 10	—	0.1.16	- 23	12
200	+ 23	18	$\bar{5}06$	- 50	53	021	- 1	—
300	- 11	7	$\bar{5}08$	- 36	49	022	+ 46	45
400	+ 55	54	$\bar{5}.0.10$	- 53	58	023	+ 58	59
500	- 37	56	602	+ 11	—	024	+ 15	16
600	+ 40	22	604	+ 39	17	025	- 40	50
700	0	—	608	+ 40	19	026	+ 21	20
800	+ 34	18	$\bar{6}02$	- 2	—	027	+ 29	19
002	+ 44	40	$\bar{6}04$	+ 36	31	028	+ 26	15
004	- 7	15	$\bar{6}06$	- 2	—	029	- 11	—
006	- 16	21	$\bar{6}08$	+ 56	50	0.2.10	+ 32	22
008	+ 76	81	$\bar{6}.0.10$	0	—	0.2.11	+ 23	13
0.0.10	+ 22	25	$\bar{6}.0.12$	+ 11	—	0.2.12	+ 11	—
0.0.12	+ 40	31	$\bar{6}.0.14$	- 1	—	0.2.13	- 10	—
0.0.14	- 3	—	$\bar{6}.0.16$	+ 32	24	0.2.14	+ 20	15
0.0.16	+ 32	12	702	- 23	—	031	- 20	22
102	- 110	75	704	- 11	—	032	- 24	12
104	- 37	41	$\bar{7}02$	- 35	20	033	- 39	43
106	- 67	65	704	- 1	—	034	- 25	29
108	- 9	9	$\bar{7}06$	- 29	17	035	+ 6	—
1.0.10	- 21	—	708	- 8	—	036	- 41	31
1.0.12	- 19	14	$\bar{7}.0.10$	- 24	12	037	+ 6	8
1.0.14	- 46	23	$\bar{7}.0.12$	- 5	—	038	+ 14	11
102	- 31	31	$\bar{7}.0.14$	- 32	19	039	+ 10	9
104	- 22	19	802	+ 3	—	0.3.10	- 25	—
106	- 25	25	804	+ 31	—	0.3.11	- 8	—
108	+ 1	—	$\bar{8}02$	- 5	—	0.3.12	- 21	18
1.0.10	- 46	31	$\bar{8}04$	+ 24	—	0.3.13	0	—
202	- 1	—	$\bar{8}06$	+ 5	—	0.3.14	- 30	20
204	+ 79	77	$\bar{8}08$	+ 42	39	041	+ 10	0
206	+ 10	—	$\bar{8}.0.10$	+ 9	—	042	+ 46	33
208	+ 40	28	$\bar{8}.0.12$	+ 33	26	043	+ 1	0
2.0.10	+ 3	—	$\bar{8}.0.14$	+ 21	—	044	- 4	0
2.0.12	+ 39	30	$\bar{8}.0.16$	+ 27	15	045	+ 15	12
$\bar{2}02$	- 14	16	902	- 23	—	046	+ 22	9
$\bar{2}04$	+ 67	68	904	- 9	—	047	- 25	18
$\bar{2}06$	- 45	57	$\bar{9}02$	- 27	—	048	- 2	0
$\bar{2}08$	+ 50	50	$\bar{9}04$	- 20	23	049	+ 2	0
$\bar{2}.0.10$	+ 5	—	906	- 34	26	0.4.10	+ 35	21
$\bar{2}.0.12$	+ 34	22	908	- 1	—	0.4.11	- 4	0
302	- 36	22	$\bar{9}.0.10$	- 32	19	0.4.12	+ 11	11
304	- 16	17	010	- 101	84	0.4.13	+ 6	0
306	- 14	—	020	+ 15	—	0.4.14	+ 26	15
308	+ 12	—	030	+ 19	19	051	- 12	0
3.0.10	- 38	16	040	+ 10	—	052	- 27	19
302	- 62	68	050	- 12	—	053	+ 16	9
304	+ 11	—	060	+ 39	26	054	- 23	19
306	- 28	22	070	- 26	—	055	- 9	0
308	- 19	18	080	+ 20	18	056	- 17	14
$\bar{3}.0.10$	- 45	40	011	+ 25	24	057	+ 13	0
$\bar{3}.0.12$	- 22	29	012	- 67	63	058	- 14	10
$\bar{3}.0.14$	- 35	27	013	- 25	16	059	- 7	0
402	+ 4	—	014	- 41	38	0.5.10	- 18	11
404	+ 68	64	015	+ 11	—	061	+ 11	0
406	+ 9	—	016	- 16	12	062	+ 8	0
$\bar{4}02$	- 6	—	017	- 2	—	063	- 13	0
404	+ 82	81	018	- 45	34	064	+ 25	15
406	+ 23	27	019	- 10	8	065	+ 10	0
408	+ 32	35	0.1.10	- 19	12	066	+ 13	11
4.0.10	+ 4	—	0.1.11	- 26	13	067	- 8	0
4.0.12	+ 70	71	0.1.12	- 28	10	068	+ 29	23
502	- 74	74	0.1.13	+ 12	—	084	+ 19	18
504	+ 13	—	0.1.14	- 14	11	088	+ 18	14
502	- 16	—	0.1.15	- 8	—			

the y co-ordinates of the potassium ions fairly accurately. Accordingly, it was decided to carry out a two-dimensional Patterson (1934) synthesis on the bc plane, using the terms $|F(0kl)|^2$. This projection gave the vector distance between the heavy chromium and potassium peaks, so that it was possible to fix the positions of the potassium ions from the known positions of the chromium atoms.

In the first approximation, then, the y and z co-ordinates of all the atoms in the unit, except the water of crystallization molecules, were used to calculate the

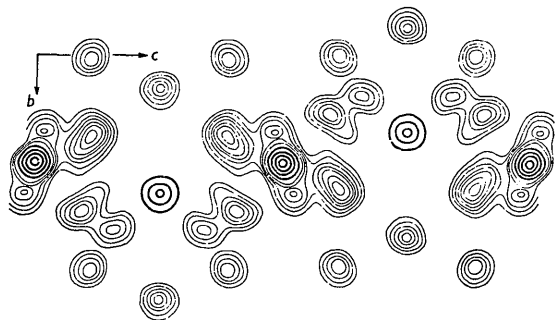


Fig. 4. Fourier projection of the structure on to the bc plane viewed against the a axis. Contours at arbitrary intervals. The heavy contour lines, drawn at higher intervals, show the positions occupied by the potassium and the chromium atoms.

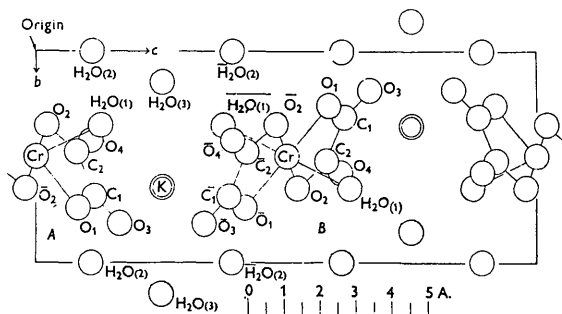


Fig. 5. Projection of the structure, viewed against the a axis, on to the bc plane. Double circles indicate that such atoms lie at distances $\frac{1}{2}a$ above or below the chromium atoms.

signs of $F(0kl)$. These calculated signs and the observed values of $F(0kl)$ were then used in evaluating the double series $\sigma(y, z)$. From the projection so obtained, considered in conjunction with the ac projection, a new set of y co-ordinates were obtained, this time using all the relevant atoms, and the series was evaluated for a second time. The fourth and final projection is shown in Fig. 4, which may be interpreted with the aid of Fig. 5. The agreement between $F(0kl)$ observed and calculated, shown in Table 1, is again quite good. It is again only for the high-order spectra that any serious discrepancies are found, where in general the observed values are smaller than the calculated ones.

Estimation of parameters

Except for the two carbon atoms in the oxalato groups, all the atoms of the formula unit were clearly resolved

on the ac projection, so that their x and z parameters could be estimated quite accurately. By comparing the positions of the oxygen atoms on this projection with our solid models of $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$, it was possible to find a position in space for the models which gave a projection consistent with the ac projection. From such a position of the models the projected C-C distance was calculated, and by transferring this calculated projected distance to the ac projection it was possible to assign x and z parameters to the two carbon atoms in an oxalato group.

As was to be expected, the resolution of atoms on the bc projection was not very good. Most of the atoms did however resolve, and in such cases the z parameters estimated from this projection were found to agree very well with those estimated from the ac projection. For these resolved atoms the y parameters could be estimated quite accurately. In the case of the unresolved atoms, those marked $\text{C}_1, \text{C}_2, \text{O}_1, \text{O}_4$ and $\text{H}_2\text{O}_{(1)}$ in Fig. 5, the z parameters were taken as known from the ac projection. Again considering the bc projection in conjunction with our solid models, it was possible to assign y parameters to the five atoms under discussion in such a way as to be consistent with the projection obtained on the bc plane (Fig. 4). The excellent agreement obtained for interatomic distances and bond angles calculated from the x, y and z parameters, showed that the procedures adopted in estimating parameters were fully justified.

Finally, it must be pointed out that, as the carbon atoms were unresolved in both projections, the final parameters of these atoms are probably not as reliable as those of the other atoms in the formula unit.

A list of parameters is given in Table 2.

Table 2. Final parameters

	x/a	y/b	z/c
Cr	0.500	0.500	0.000
K	0.000	0.645	0.250
O_1	0.451	0.741	0.083
O_2	0.296	0.350	0.021
O_3	0.256	0.816	0.171
O_4	0.109	0.423	0.109
C_1	0.318	0.687	0.115
C_2	0.232	0.476	0.080
$\text{H}_2\text{O}_{(1)}$	0.667	0.350	0.128
$\text{H}_2\text{O}_{(2)}$	0.867	1.000	0.112
$\text{H}_2\text{O}_{(3)}$	0.500	0.147	0.250

Description of the complex ion $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$

In Fig. 6 the dimensions of the complex ion, as calculated from the parameters shown in Table 2, are given. The chromium atom lies at the symmetry centre of the complex ion. Within the errors of experiment the two oxalato groups lie in a single plane. The two water molecules of the complex ion are perpendicular to this plane. The four oxygen atoms and two water molecules surrounding the chromium atom form an approximate octahedral arrangement, as can be seen from the distances given. The angles $\text{O}_1\text{-Cr-O}_2$ and $\text{O}_1\text{-Cr-O}_2$ are,

however, not equal to 90° , as a true octahedral arrangement would imply, and this seems to indicate that the oxalato group has a fairly rigid structure which does not change when it is joined to a central chromium atom. The rather longer distance of 2.02 Å. between Cr and $H_2O_{(1)}$, as compared with distances 1.92–1.93 Å. for the other oxygen atoms surrounding the chromium atom, may be indicative of the dipole character of the former type of bond.

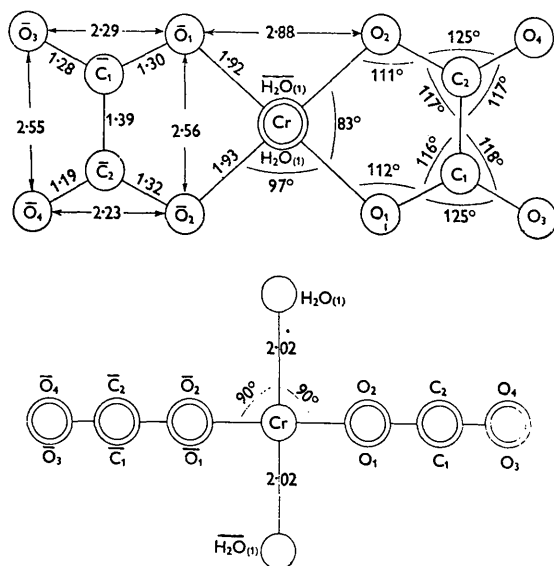


Fig. 6. Dimensions of the complex ion $[Cr(C_2O_4)_2(H_2O)_2]$.

The C–C distance of 1.39 Å., although not very reliable because the carbon atoms were not fully resolved in either projection, approaches the corresponding distance 1.43–1.45 Å. found by Robertson & Woodward (1936) for oxalic acid, and, as there, seems to indicate a partial double-bond character between such atoms. The C–O distances approach a mean value of 1.30 Å., except for the C_2-O_4 distance which is only 1.19 Å. This may, however, not be a real difference and may be due to the fact that the C_2 and O_4 atoms were not completely resolved on the bc projection. The angles $O_1-C_1-O_3$ and $O_2-C_2-O_4$ are 125° , in good agreement with Robertson's value of 126° .

The packing of the formula units in the crystal, and the bonding

The packing and bonding of the formula units in the crystal are best illustrated by referring to Fig. 7, which may be compared with Fig. 3. The plane of a complex ion $[Cr(C_2O_4)_2(H_2O)_2]$ is inclined to the ac plane at an angle of 61° , while the long symmetry axis of the complex ion makes an angle of 9° with its projection on the ac plane. Such symmetry axes of the complex ions are directed towards the potassium ions, which lie on two-fold axes perpendicular to the paper. The potassium ions lie at distances of 0.83 Å. above or below the plane of the paper. The closest distances of approach between

complex ions, disregarding for the present bonds exhibited by the water molecules of such ions, which will be discussed later, are found between oxygen atoms belonging to two neighbouring ions in the b direction. Such distances approach the average value 3.70 Å., and they are approximately in the b direction.

Referring to Fig. 7, it is evident that complex ions of the type A and B and the potassium ions form what can be regarded as corrugated chains running through the structure in directions approximately parallel to the (102) crystal planes. The bonds between members of such chains are ionic. The average length of these bonds, between the terminal oxygen atoms (marked 3, 4, $\bar{3}$, $\bar{4}$) of the complex ions and the potassium ions, is 2.74 Å. Such bonds are shown as full arrows in Fig. 7.

Referring again to Fig. 7, consideration will show that neighbouring chains, of the type discussed above, have reversed corrugations. This is due to the glide plane lying in the plane of the diagram. Both hydrogen and ionic bonds are found between such neighbouring chains. A water molecule (1 or $\bar{1}$) belonging to a complex ion forms one ionic link between neighbouring chains, inasmuch as it is one of the eight oxygen atoms surrounding a potassium ion. The bond distance here is 3.10 Å., and because of its weaker character it is not shown in the diagram. The other water molecule (2 or $\bar{2}$) surrounding a potassium ion approaches it to within a distance of 2.74 Å. to form an ionic bond, and this water molecule is also linked by a hydrogen bond of length 2.75 Å. to one of the inner complex oxygen atoms ($\bar{2}$) of a neighbouring chain. Full arrows again indicate this type of bonding. Neighbouring chains are further linked by the third water molecule (3) of the formula unit. This water molecule is linked to two complex water molecules (1 and $\bar{1}$) belonging to neighbouring chains by hydrogen bonds of length 2.72 Å. This is again illustrated by full arrows. In the ways outlined above the chains are linked together firmly to form a kind of layer-like structure. The full arrows in Fig. 7 represent the bonds within such layers.

We must next consider the binding forces between adjacent layers. Fig. 7 shows the projection of such a layer along b on to the ac plane, so that perpendicularly above this layer, and at a distance b , lies an identical layer. It is found that two different kinds of water molecules are mainly responsible for the bonding between adjacent layers. The first kind (2 or $\bar{2}$), which is linked to a potassium ion and an inner oxygen ($\bar{2}$) of a complex ion in one layer, is also linked to a complex water molecule (1) and to one terminal oxygen (4) in the layer immediately above. The two latter bonds are both hydrogen bonds of lengths 2.66 and 3.04 Å. respectively, and they are shown by dotted arrows. The second kind of water molecule (3), which is linked by two hydrogen bonds of length 2.72 Å. to two complex water molecules (1 and $\bar{1}$) lying in one layer, is also linked to two terminal oxygen atoms (3 and $\bar{3}$) in an adjacent layer. These are again hydrogen bonds of length 2.65 Å., also

shown by dotted arrows. The bonds formed by these two kinds of water molecules are found to be approximately tetrahedral, two arms of the tetrahedron being fixed to one layer and the other two arms to the next layer above. For each formula unit there are two water molecules of the first kind and one of the second kind, so that a complex ion in one layer is linked to complex ions in the next layer by three hydrogen bond bridges through three water molecules.

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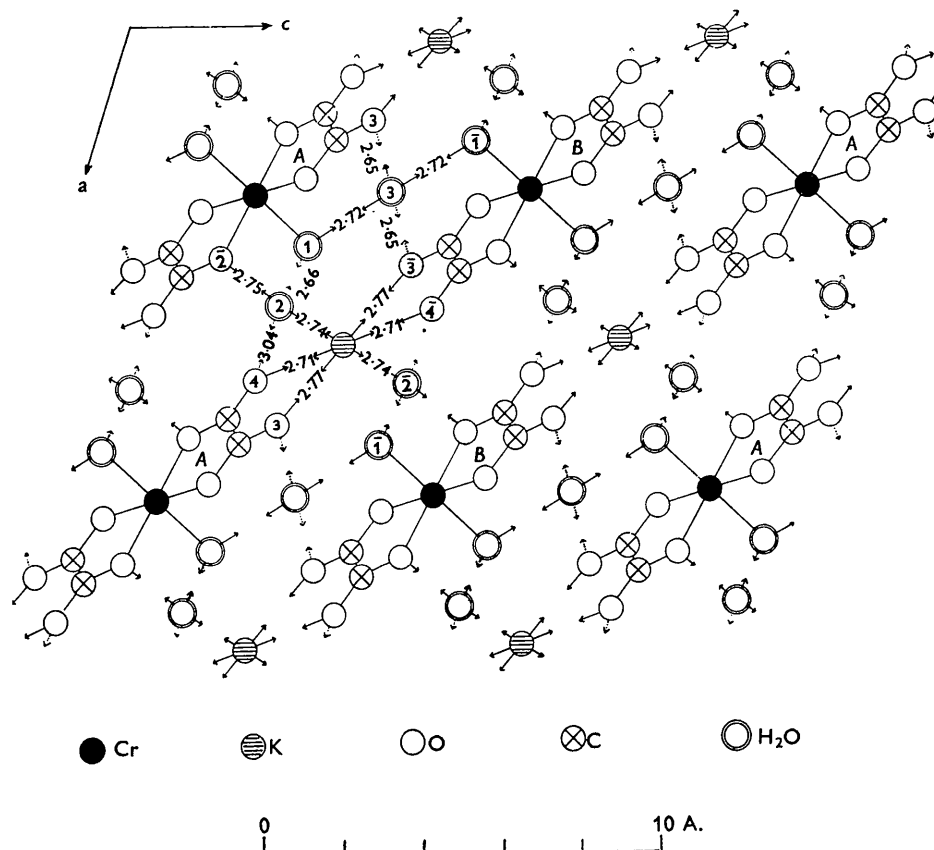


Fig. 7. Projection of the structure in the direction of the b axis on to the ac plane. Units marked B are derived from those marked A by the operation of a glide plane parallel to (010) . The chromium atoms lie on the glide plane.

The fact that hydrogen bonds only exist between the layers, whereas both hydrogen and ionic bonds exist in the layers, may account for the stronger nature of the hydrogen bonds between layers, where such bonds tend to a value 2.65 Å, as compared with a value of about 2.74 Å, in layers. The crystals are hard and difficult to cleave, indicating that the bonds discussed in this section must hold the structure together quite firmly.

Finally, it may be pointed out that there appear to be holes in the structure, between two potassium ions and two chromium atoms (Fig. 7), seemingly large enough to accommodate another water molecule. The positions referred to, however, are symmetry centres, so that, even if there were enough room, the tetrahedral configuration of the water molecule immediately rules out this possibility.

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